Photocatalytic oxidation of aliphatic and aromatic sulfides in the presence of silica adsorbed or zeolite-encapsulated 2,4,6-triphenyl(thia)pyrylium

Sergio M. Bonesi [a,b], Esther Carbonell [c], Hermenegildo Garcia [c],
Maurizio Fagnoni [b], Angelo Albini [b,*]

[a] *CIHIDECAR-CONICET, Departamento de Química Orgánica, Pabellón II, Ciudad Universitaria, Int. Güiraldes s/n,
Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires, 1428 Buenos Aires, Argentina*
[b] *Dipartimento di Chimica Organica, Università, via Taramelli 10, 27100 Pavia, Italy*
[c] *Instituto de Tecnologia Quimica CSIC-UPV, Universidad Politecnica de Valencia, av. De los Naranjos s/n, 46012 Valencia, Spain*

Abstract

Solid photocatalysts in which the 2,4,6-triphenylpyrylium (TP) or 2,4,6-triphenylthiapyrylium cation (TTP) are encapsulated within zeolite Y or deposited on mesoporous silica are used as photosensitizers for the oxidation of sulfides, both aromatic and aliphatic, in solvents of various polarity. Contrary to the same cations in solution, these solid sensitizers are not significantly degraded during operation. An effective oxygenation takes place leading to sulfoxides, disulfides, sulfinic and sulfenic esters as well as sulfonic acids. This large scope method shows a limited dependence on the substrate structure and on conditions and is suitable for the abatement of sulfur-containing pollutants.
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1. Introduction

Photosensitized oxygenation is a typical 'advanced oxidation method', characterized by the environmentally friendly conditions [1]. The key step in such reactions, activation of oxygen, occurs according to different mechanisms, typically involving singlet oxygen, superoxide anion or hydroxyl radicals [2]. A main problem in every case is that the sensitizers themselves are liable to the action of such reactive oxygen species and are consumed at a rate comparable to that of the substrates. Therefore one loses one of the key advantages of a photosensitized process, that is that only a minimal amount of a chemical, the sensitizer, has to be added. This limitation does not apply to inorganic materials, in particular to largely used semiconductor oxides [3–5]. An alternative choice is protecting the organic sensitizers by immobilizing in the cavities of a solid support [6–17]. This arrangement combines the better control

of the reaction typical of organic sensitizer with the robust nature of heterogeneous photocatalyst.

The purpose of this work is twofold, on one hand testing the efficiency and the stability of some immobilized photocatalysts based on the (thia)pyrylium cation in oxidation processes even when operating on a relatively large amount of substrates and on the other one assessing the usefulness of such materials in an application of practical significance, that is the oxidation of sulfides. This is a process of interest in various fields, from synthetic chemistry (oxidation to sulfoxides reverts the electronic character of the sulfide moiety and introduces a stereocenter) to the modeling of biochemical oxidations. From the environmental point of view, serious problems are the desulfurization of fossil fuels [18], the removal of foul smelling sulfides from exhaust of various nature, from meat rendering plants [19] to industrial wastewater treatment plants [20] and the disposal of sulfur-containing chemical warfare agents [21].
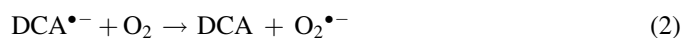
Oxidative desulfurization by various reagents has been studied extensively in recent years for such applications [22–25]. As an example, a high conversion of sulfides to sulfones and sulfoxides provides a difference in polarity that

* Corresponding author. Tel.: +39 0382 987316; fax: +39 0382 987323.
E-mail address: angelo.albini@unipv.it (A. Albini).

can be used for the selective removal of such substances with solid adsorbents, in order to obtain fuel that meets the increasingly stringent purity standards and avoid damage to catalytic converters [26].

Although effective procedures have been reported, some limitations remain and at any rate the ideal method should use directly oxygen, rather than introducing a potentially polluting reactant such as a strongly oxidizing chemical agent, and be characterized by mild conditions and general application. Photochemistry may be a sensible choice, in particular if a photosensitized method is used that is effective under solar light. The extensively investigated dye-sensitized ('Type II') oxidation via singlet oxygen [2,27,28] satisfies this requirement, but is effective only with aliphatic sulfides in protic solvents [29–31] (while, e.g. for desulfurization of fuels aromatic sulfides are even more important than the aliphatic ones and the medium is nonpolar). Titanium dioxide has been used in solution for (hetero)aromatic sulfides [32] and in the gas phase for aliphatic derivatives, where deactivation of the photocatalyst occurred, however [33]. The use of different organic photosensitizers may enlarge the scope of the reaction. Thus, with an electron-withdrawing substituted aromatic, e.g. 9,10-dicyanoanthracene (DCA), oxidation of aromatic sulfides was obtained via an alternative path, that is an electron transfer (ET) and generation of superoxide (Eqs. (1)–(3)) [34–37].

$$^1DCA + RR'S \rightarrow DCA^{\bullet-} + RR'S^{\bullet+} \tag{1}$$

$$DCA^{\bullet-} + O_2 \rightarrow DCA + O_2^{\bullet-} \tag{2}$$

$$RR'S^{\bullet+} + O_2^{\bullet-} \rightarrow RR'SO \tag{3}$$

In order that this mechanism operates, the sulfide concentration must be sufficiently high as to effectively quench the short-lived singlet excited DCA (Eq. (1)), since spontaneous intersystem crossing (ISC) to the long-lived triplet is inefficient. At high sulfide concentration, quenching of the singlet yield ^{3}DCA and thus an efficient oxidation (quantum yield up to 2) may take place, but this may be a limitation when a low concentration of sulfides is used [36,38]. Ideally, a general method should be able both to degrade a large amount of the pollutant and to reach a very low residual concentration. For this aim pyrylium salts (P^+) are better suited, since they are characterized by a rather efficient ISC, and not only the singlet (τ_S 2.9 ns) but also the triplet (τ_T ca. 10 μs) can operate as an oxidant [39,40]. With adamantyleneadamantane these sensitizers have been demonstrated to induce ET either to the singlet or to the triplet according to the substrate concentration [39]. Both states are good enough oxidants for accepting an electron from sulfides (see Eqs. (4) and (5)).

$$^1P^+ + RR'S \rightarrow P^{\bullet} + RR'S^{\bullet+} \tag{4}$$

$$^3P^+ + RR'S \rightarrow P^{\bullet} + RR'S^{\bullet+} \tag{5}$$
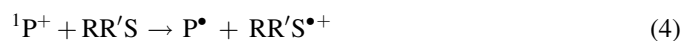
Indeed, pyrylium salts absorb blue light and cause sulfoxidation with reasonable efficiency (with both aromatic and aliphatic sulfides), although the mechanism has not yet clearly determined because, differently from the DCA$^{\bullet-}$ case, reduction of

oxygen by $P^{\bullet}$ is ineffective [35,36]. Possibilities that have been considered are a reaction of the sulfide radical cation directly with oxygen (Eq. (6)) and the formation of some oxygen adduct from $P^{\bullet}$, which then is the active species in the oxidation (Eqs. (7) and (8)).

$$RR'S^{\bullet+} + O_2 \rightarrow RR'SO \tag{6}$$

$$P^{\bullet} + O_2 \rightarrow PO_2^{\bullet} \tag{7}$$

$$PO_2^{\bullet} + RR'S \rightarrow RR'SO \tag{8}$$

Apart from mechanistic problems, the limitation to the practical application of P^+ for sulfoxidation is that such materials are photolabile, a common shortcoming with organic sensitizers, as mentioned above, which is even more important in this case. One of the ways for overcoming this limitation is incorporating the sensitizer into a solid phase, as indeed has been done for other photosensitizers of various classes, both by covalent bonding and by different complexation and trapping. Pyrylium salts trapped in zeolites have been first tested by some of the present authors, mainly with thianthrene with a starting concentration around 100 ppm [15,16]. Developing this hint, we carried out a comprehensive study of the photooxidation of aliphatic and aromatic sulfides by using some solid phase incorporated pyrylium salts, higher starting concentrations and in different solvents.

2. Experimental

2.1. Preparation and characterization of the photocatalysts

SiO$_2$ (Basf, 200 m^2 g^{-1}) and the zeolite HY (PQ CBV 720) were commercial samples. MCM-41 (Si/Al 13) was synthesized according to a known experimental procedure by using cetyltrimethylammonium bromide and an aerosil and alumina as silicon and aluminum source, respectively [41,42]. The crystallinity of MCM-41 samples was determined by powder X-ray diffraction. The surface area was measured by isothermal N$_2$ adsorption using a Micrometrics 2000 ASAP apparatus.

The tetrafluoroborate of 2,4,6-triphenylpyrylium (TPT) was supplied by Aldrich and the thia analogue TTP perchlorate was synthesized by reacting TP$^+$ with SH$^-$ as reported in the literature [43,44]. TP$^+$ on silica and TP$^+$ on MCM-41 were prepared by depositing from a dichloromethane solution given amounts (4% loading) of TP$^+$ onto thermally dehydrated (120 °C, 2 h) silica or MCM-41.

TPT–HY was prepared starting from commercial HY by following the reported procedure [16]. For preparing TTPT–HY a solution of chalcone (21 mg) and acetophenone (12 mg) in cyclohexane (10 mL) saturated of H$_2$S was magnetically stirred in the presence of thermally dehydrated (500 °C) HY at reflux temperature for 3 days while a constant stream of H$_2$S was flowed through the system according to the method reported in the literature [6]. During the ship-in-the-bottle synthesis the solid became increasingly orange in color. After this time, the raw solid photocatalyst was submitted to

exhaustive solid–liquid extraction using at Soxhlet apparatus and dichloromethane as the solvent.

The solids were characterized by combustion chemical analysis (Fisons CHNS analyzer) and spectroscopy techniques. Diffuse reflectance UV–vis spectra were recorded in a Cary 5G spectrophotometer with an integrated sphere using $BaSO_4$ as standard. FTIR spectra were recorded in a Nicolet 710 spectrophotometer using sealed greaseless CaF_2 cells. The self-supported wafers (10 mg) were prepared by pressing the powders at 2–3 tonnes cm^{-2} for 1 min. The IR spectra were recorded at room temperature after outgassing the samples at 200 °C under 10^{-2} Pa for 1 h.

2.2. Photosensitized oxidation of sulfides 1a–e

Sulfide **1d** was prepared according to a literature procedure [45]. The other sulfides and the solvents were high-purity commercial samples and were used as received. The photo-reaction was carried out in Pyrex tubes by using a final volume of 2 mL of 0.01–0.05 M solutions of the sulfides in the appropriate solvent and in the presence of 6 mg of the photosensitizer (zeolite encapsulated or MCM adsorbed TPT or TTPT). Then, 50 μL of an appropriate internal standard was added. The tubes were rubber-stoppered and magnetically stirred for 15 min in the dark. Then, the tubes were exposed to four 15 W phosphor-coated lamps (applied photophysics) centered at 410 nm, while a stream of dry oxygen saturated with the appropriate solvent was passed in the solution through a needle (temperature 20 ± 1 °C). The solution was periodically subjected to chromatographic analysis and the photoproducts were determined by HPLC (Suprasyl RP-18 chromatographic column, UV detector—λ: 230 or 260 nm, eluent: $MeCN–H_2O$ (9:1) or (8:2) depending on the sulfide studied) on the basis of calibration curves with authentic samples in the presence of biphenyl as the internal standard.

When the photoreactions were carried out under homogeneous conditions, 200 μL of 0.10 M solution of the sulfide in the chosen solvent was mixed with 100 μL of 1×10^{-3} M solution of the photosensitizer (TPT or TTPT) and with 50 μL of 0.10 M solution of biphenyl. Then, a final volume of 2 mL was build up with the same solvent. The irradiations procedure and chromatographic analysis were carried out as described above.

The oxidized compounds for comparison with the products from the photosensitization were prepared according to published procedures (Et_2SO [46], $PhCH_2SOEt$ [46], Ph_2SO [47], EtSOSEt [48,49], $EtSO_2Set$ [50] and $PhSO_2SPh$ [51]) or were of commercial origin. The radiation intensity, measured by taking the photosensitized oxidation of 1,2-diphenylethylene as the actinometer, was of ca. 1×10^{-6} Einstein cm^{-2} min^{-1}.

3. Results and discussion

The sensitizers considered were 2,4,6-triphenylpyrylium tetrafluoroborate (TPT) and the sulfur analogue, 2,4,6-triphenylthiapyrylium tetrafluoroborate (TTPT), which is even more easily reduced than TPT [52] The sulfides considered for

the photooxygenation were two dialkyl derivatives, diethyl sulfide (**1a**) and benzyl ethyl sulfide (**1b**), two aryl alkyl derivatives, thioanisole (**1c**) and *tert*-butyl phenyl sulfide (**1d**) and the diaryl derivative diphenyl sulfide (**1e**, see Fig. 1). Furthermore, the solvent effect was explored, both because in ET sensitized oxidations this may be a significant factor, as indicated from previous studies and in order to model the application both in less polar media (for modeling the desulfurization of oil) and in polar media (for modeling the application to waste recover). 1,2-Dichloroethane (DCE), acetonitrile and methanol were routinely tested in the systems studied. In order to explore the limits of the method, relatively high starting concentrations of the sulfides were used (0.01–0.05 M). In all of the cases 'blue' light (phosphor-coated lamps with centre of emission 410 nm) was used.

Preliminary tests showed that all of the sulfides (0.01 M) were oxidized when either TPT or TTPT were used as homogeneous sensitizers, but the last compounds were consumed, most rapidly in methanol, and in this case their concentration had to be restored by adding further portions in order to completely convert the sulfides.

Solid materials in which the above sensitizers were incorporated in various ways were prepared and tested (see Table 1). In one of such samples the TPT molecule had been synthesized within the cavity of a zeolite HY (Si/Al 2.4 ratio, 340 m^2 g^{-1} surface area) through a ship-in-the-bottle synthesis from chalchone and acetophenone (this is indicated as TPT–HY) [6,15,16]. In the presence of H_2S a similar TTPT containing zeolite was prepared (TTPT–HY). A different material contained TPT adsorbed (40 mg g^{-1}) inside the mesopores (3.4 nm) of structured, periodic silica (MCM-41) with an extremely large surface area (950 m^2 g^{-1}) (TPT–MCM). Finally, the same amount of sensitizer physically adsorbed on silica gel (SG) was used (TPT–SG). The materials were characterized by combustion analysis, as well as diffuse reflectance UV–vis and IR spectroscopy, confirming the presence of the chromophore, as previously reported in detail [6]. These materials were added to the sulfide solution (0.05 M) and irradiated under stirring. In the case of the silica gel samples, the sensitizer was released in solution, as determined by UV–vis spectroscopy of the supernatant solution, while in the other cases there was no detectable release over 10 h.
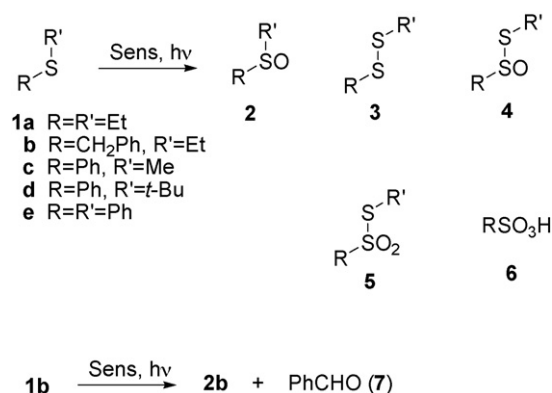

Fig. 1. Products formed from the sensitized oxidation of sulfides 1.

Table 1
Photosensitizers tested

Acronym		Support	Surface area ($m^2\,g^{-1}$)	Preparation	Pores (μm)
TPT	Homogeneous				
TPT–HY	Heterogeneous	Zeolite HY	340	Ship-in-the-bottle synthesis	0.74
TPT–MCM	Heterogeneous	Mesoporous silica	950	Adsorption	3.4
TPT–SG	Heterogeneous	Silica gel	210	Adsorption	
TTPT	Homogeneous				
TTPH–HY	Heterogeneous	Zeolite HY	340	Ship-in-the-bottle synthesis	0.74

All of the above materials were active in the photooxidation and, apart from the case of TPT–SG, from which the sensitizer was washed away, appeared to be much more resistant to irradiation than the homogenous sensitizers showing no significant bleaching after several hours irradiation. Samples of TPT–HY were recovered and reused for two further oxidations showing no significant loss of activity. The reaction of the sulfides proceeded regularly and the material balance was good in most cases. The products formed (see Fig. 1 and Table 2) were the corresponding sulfoxides accompanied by compounds arising from the oxidative cleavage of (one of) the C–S bonds. In particular, from diethyl sulfide (1a) the sulfoxide (2a) was accompanied by the disulfide (3a), the thiosulfinate (4a) and the thiosulfonate (5a) along with

Table 2
Product distribution from the photooxidation of sulfides 1a–d with dissolved and heterogeneous sensitizers in various solvents

Sulfide	Solvent	Sensitizer	Products[a]	
			C–S bond cleavage	Conserving the skeleton
Et$_2$S, 1a	MeOH	TPT–HY	EtSO$_3$H, 27; EtSOSEt, 11; EtSO$_2$SEt, 8; EtS$_2$Et, 6	EtSOEt, 11
		TPT–MCM	EtSO$_3$H, 11; EtSOSEt, 13; EtSO$_2$SEt, 13; EtS$_2$Et, 14	EtSOEt, 48
		TTPT–HY	EtSO$_3$H, tr; EtSOSEt, 10; EtSO$_2$SEt, 10; EtS$_2$Et, 10	EtSOEt, 58
	MeCN	TPT–HY	EtSO$_3$H, 40; EtSO$_2$SEt, 11; EtS$_2$Et, 11	EtSOEt, 37
		TPT–MCM	EtSO$_3$H, 34; EtSO$_2$SEt, 36; EtS$_2$Et, 9	EtSOEt, 19
		TTPT–HY	EtSO$_3$H, 24	EtSOEt, 75
	DCE	TPT–HY	EtSO$_3$H, 47	EtSOEt, 44
		TPT–MCM	EtSO$_3$H, 30	EtSOEt, 41
		TTPT–HY	EtSOSEt, 3; EtSO$_2$SEt, 10; EtS$_2$Et, 9	EtSOEt, 73
PhCH$_2$SEt, 1b	MeOH	TPT–HY	PhCHO, 6; PhCH(OMe)$_2$, 1	PhCH$_2$SOEt, 62
		TPT–MCM	PhCHO, tr; PhCH(OMe)$_2$, 5	PhCH$_2$SOEt, 36
		TTPT–HY	PhCHO, 12	PhCH$_2$SOEt, 51
	MeCN	TPT–HY	PhCHO, 28	PhCH$_2$SOEt, 69
		TPT–MCM	PhCHO, 24	PhCH$_2$SOEt, 64
		TTPT–HY	PhCHO, 18	PhCH$_2$SOEt, 35
	DCE	TPT–HY	PhCHO, 21	PhCH$_2$SOEt, 54
		TPT–MCM	PhCHO, 23	PhCH$_2$SOEt, 49
		TTPT–HY	PhCHO, 18	PhCH$_2$SOEt, 85
PhSMe, 1c	MeOH	TPT–HY	PhSO$_3$H, 14; PhSO$_2$SPh, 7; PhS$_2$Ph, 6	PhSO–Me, 69
		TPT–MCM	PhSO$_3$H, tr; PhSO$_2$SPh, 3	PhSO–Me, 83
		TTPT–HY	PhSO$_3$H, tr; PhSO$_2$SPh, 16	PhSO–Me, 68
	MeCN	TPT–HY	PhSO$_3$H, 2; PhS$_2$Ph, 18	PhSO–Me, 48
		TPT–MCM	PhSO$_3$H, 15; PhS$_2$Ph, 5	PhSO–Me, 79
		TTPT–HY	PhSO$_3$H, 2	PhSO–Me, 85
	DCE	TPT–HY	PhSO$_3$H, tr; PhS$_2$Ph, 61	PhSO–Me, 17
		TPT–MCM	PhSO$_3$H, 3; PhS$_2$Ph, 29	PhSO–Me, 42
		TTPT–HY	PhS$_2$Ph, 8	PhSO–Me, 52
PhS-t-Bu, 1d	MeOH	TPT–HY	PhSO$_3$H, 10; PhSO$_2$SPh, 10; PhS$_2$Ph, 33	PhSO-t-Bu, 23
		TPT–MCM	PhSO$_3$H, 12; PhSO$_2$SPh, 23; PhS$_2$Ph, 32	PhSO-t-Bu, 12
		TTPT–HY	PhSO$_3$H, 12	PhSO-t-Bu, 73
	MeCN	TPT–HY	PhSO$_3$H, 8; PhS$_2$Ph, 50	PhSO-t-Bu, 12
		TPT–MCM	PhSO$_3$H, 12; PhSO$_2$SPh, 23; PhS$_2$Ph, 32	PhSO-t-Bu, 12
		TTPT–HY	PhS$_2$Ph, 35	
	DCE	TPT–HY	PhSO$_3$H, 10; PhS$_2$Ph, 47	PhSO-t-Bu, 26
		TPT–MCM	PhSO$_3$H, 12; PhSO$_2$SPh, 23; PhS$_2$Ph, 32	PhSO-t-Bu, 12
		TTPT–HY	PhSO$_3$H, 3; PhSO$_2$SPh, 13; PhS$_2$Ph, 13	PhSO-t-Bu, 15
Ph$_2$S	MeOH, MeCN, DCE	All of the above		Ph$_2$SO 80-90

[a] High conversion of the sulfides, >70%. Products yields based on consumed sulfides.

some ethylsulfonic acid (**6a**) (see Fig. 1). The benzyl sulfide (**1b**) underwent both sulfoxidation to **2b** and oxidative cleavage to benzaldehyde (**7**). Diphenyl sulfide (**1e**) gave only the sulfoxide in good yield, while with the aryl alkyl derivatives **1c**, **d** the sulfoxides were accompanied by the disulfide (a major product from **1d**) and lower amounts of the sulfonic acid and the thiosulfonate.

Thus, both sulfoxidation conserving the molecular skeleton and oxidative cleavage of the carbon–sulfur bond took place. The reaction was initiated by electron transfer to the excited (thia)pyrylium sensitizer P^+ leading to the sulfide radical cation and the pyryl radical (see Fig. 2a), both rather persisting species, as demonstrated by previous flash photolysis investigations [35,36].

This was followed either by direct reaction of the sulfide radical cation with oxygen to give a persulfoxide radical cation (Fig. 2b, path i) or by addition of oxygen to the pyranyl radical $P^\bullet$ to give the peroxy radical $POO^\bullet$, followed by formal transfer of superoxide to the sulfide radical cation to give the persulfoxide (path ii). Either way these oxygenated intermediates in turn underwent oxygen transfer to the sulfide giving the sulfoxide or intramolecular H-abstraction from the α position followed by shift of the hydroperoxyl group. The latter path led to C–S bond cleavage forming thiols and further oxidation products as reported in Fig. 2b, notably the disulfides that are reasonably formed via a secondary photo-induced oxidation of the thiols.

In the case the radical cation had a decomposition path accessible, this offered a further alternative, as is the case for
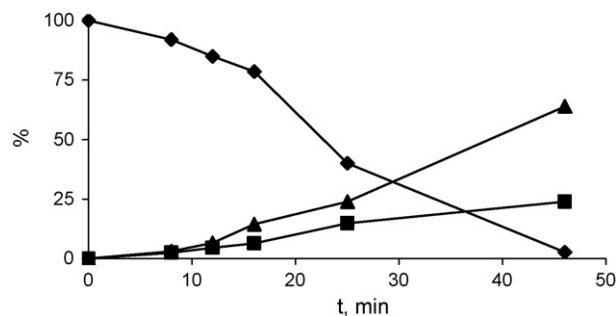

(a)

(b)

(c)

Fig. 2. Mechanistic scheme for the (thia)pyrylium (P^+) electron transfer photosensitized oxidation of sulfides.

Fig. 3. Photosensitized (TPT–HY in MeCN) oxidation of benzyl ethyl sulfide (1b, diamonds) and formation of benzyl ethyl sulfoxide (2b, triangles) and of benzaldehyde (7, squares).

benzyl sulfide **1b** where deprotonation from the radical cation has been previously documented and leads to an α-thioalkyl radical and again to a peroxy radical from it (Fig. 2c).

The product distribution was in general similar when using the dissolved sensitizers TPT and TTPT and when using the corresponding heterogeneous materials. However, some differences should be highlighted.

The most important point with regards to the application of the method was that the photosensitizing activity of the heterogeneous materials was retained for a much longer time and allowed to carry out the sensitized oxidation up to extensive or complete consumption of a relatively high concentration of the starting material (as well as to recover and reuse the sensitizer, see above). An exemplary photocatalyzed oxidation is presented in Fig. 3, where the oxidation of **1b** (0.01 M in MeCN) to give **2b** and **7** is reported. As one may see, the oxidation proceeded regularly and a good material balance was maintained. A very similar result was obtained when using molecular TPT (5×10^{-4} M) as the sensitizer. However, in that case complete conversion of the sulfide was
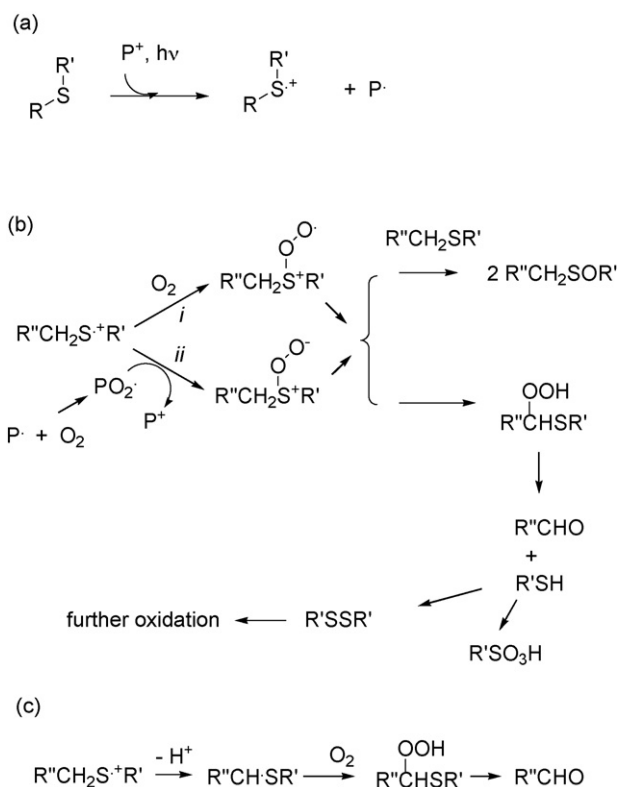
Table 3
Rate of oxidation (μmol min^{-1}, measured at <25% conversion) of sulfides **1a–e** with dissolved and heterogeneous sensitizers in various solvents

Solvent	Sensitizer			Sulfides		
	Sensitizer	Et$_2$S	PhCH$_2$SEt	PhSMe	PhS-t-Bu	Ph$_2$S
DCE	TPT	2.0	3.8	1.4	1.7	1.0
	TPT–HY	2.2	2.4	0.9	0.3	0.13
	TPT–MCM	2.0	2.9	1.4	1.2	0.7
	TPT–SG	2.1	2.3	1.9	1.2	0.6
	TTPT	3.6	4.2	2.1	1.1	0.13
	TTPT–HY	1.0	1.0	0.5	0.2	0.05
MeCN	TPT	3.3	2.8	1.0	1.5	0.8
	TPT–HY	3.7	2.7	0.6	1.3	0.04
	TPT–MCM	1.4	1.4	0.4	0.7	0.17
	TPT–SG	1.2	1.2	0.4	0.4	0.34
	TTPT	1.9	3.5	0.4	0.4	0.28
	TTPT–HY	2.8	2.4	0.2	0.2	0.06
MeOH	TPT	6.5	3.8	2.8	2.1	1.3
	TPT–HY	3.7	2.0	1.4	0.3	0.26
	TPT–MCM	4.8	1.9	1.2	0.9	0.8
	TPT–SG	4.6	1.0	0.6	1.2	0.9
	TTPT	5.2	3.2	0.4	0.2	0.2
	TTPT–HY	3.7	2.2	0.7	0.01	0.02

successful only when regenerating the absorbance by adding further portions of the sensitizer as long as this was bleached (four to five times).

Furthermore, the efficiency and the course of the reaction did depend on the sulfide structure and on conditions, at least to some extent. This point can be appreciated with reference to Table 3, where the oxidation rates (μmol converted per min) are compared (irradiations under uniform conditions at a *ca.* 25% conversion) and by taking into account that the large pore dimension of the MCM-41 silica used (3.4 nm) [6,53] allows easy diffusion of organic molecules, while the smaller dimension of the zeolite pores (0.74 nm) hinders mobility.

The key observations are as follows. The pyrylium and thiapyrylium salts photosensitized oxidations discriminate less than singlet oxygen reactions, with less difference between aryl and alkyl sulfides, and a lower solvent effect. With TPT as the dissolved sensitizer there is only a factor 5 between the fastest and the slowest sulfide among those considered here, and the change due to the solvent is within a factor of 3 (see below). This may be compared to a factor of 500 between **1a** and **1e** and

a factor of 20 between MeOH and DCE for **1a** for the reaction with singlet oxygen [29,54]. The thiapyrylium salt TTPT is more selective, with a larger difference between **1a** and **1e** (up to a factor of 25).

These characteristics applied also to zeolite immobilized sensitizers. In particular, the oxidation of a small and flexible molecule such as **1a** maintained roughly the same efficiency as with the soluble sensitizer and was little affected by the type of photosensitizer Essentially the same observations applied to the case of **1b**, again a flexible molecule.

Different is the case for aromatic sulfides **1c–e**. With these compounds accessibility of the sensitizer was an important issue. In fact, molecular modeling and docking using molecular mechanics predict that these larger sulfides should experience diffusion limitations for crossing the 0.74 nm zeolite Y cage windows. Fig. 4 shows some selected images of the docking to illustrate the relative sizes of the molecules with respect to the cavity openings. It is apparent that there is no hindering in the case of **1a**. However, these models lead to the expectation that access to the vicinity of the sensitizers, in particular with
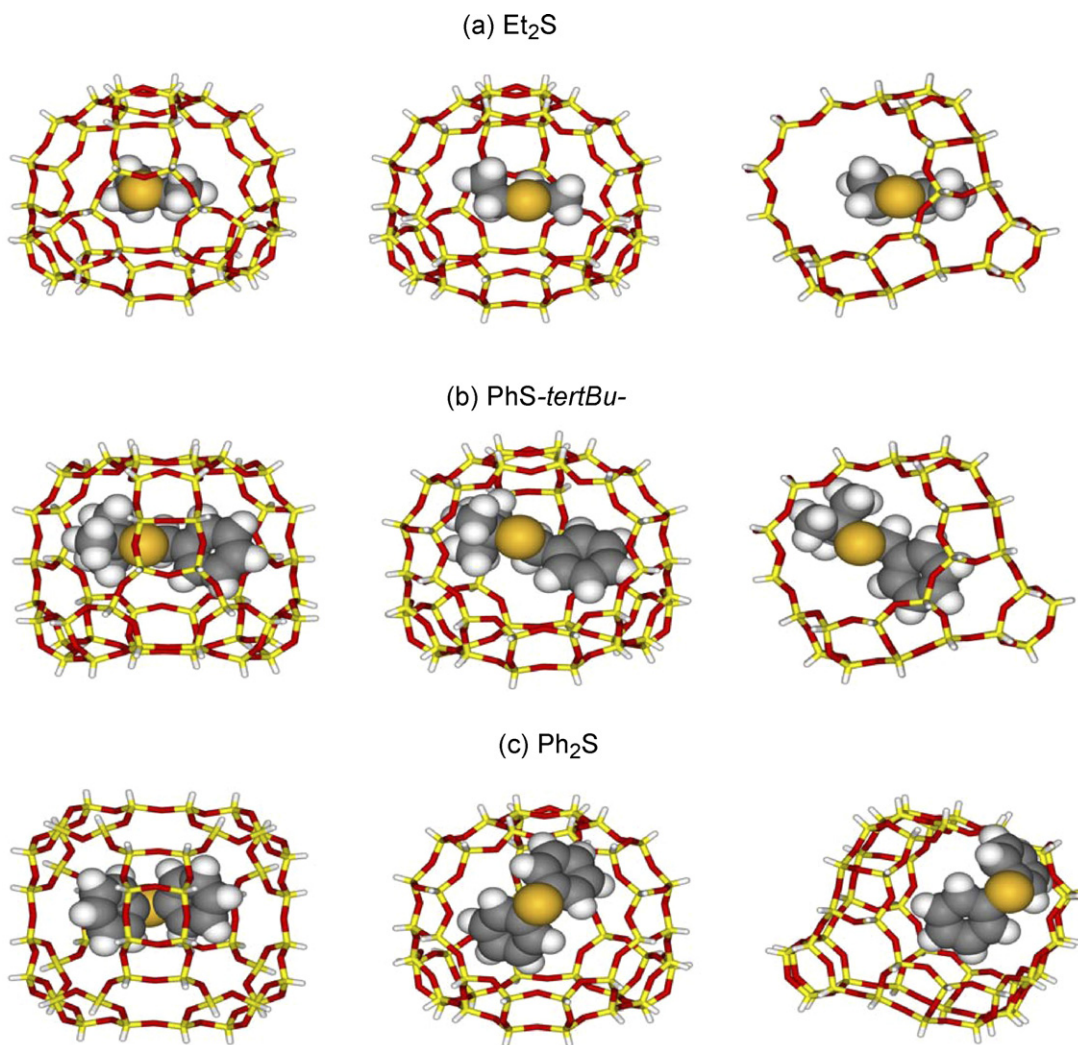
(a) Et$_2$S

(b) PhS-*tertBu-*

(c) Ph$_2$S

Fig. 4. Frontal (the cage window behind the organic molecule) and lateral views of the docking of sulfides 1a, **1d** and **1e** entering the zeolite Y supercage. For simplicity of the model, a pure siliceous cage with crystallographic positions corresponding to those of the faujasite has been used. The remarkable difference in the size with respect to the zeolite opening of these sulfides should be responsible of the difference in reactivity of the free and zeolite-encapsulated sensitizer.
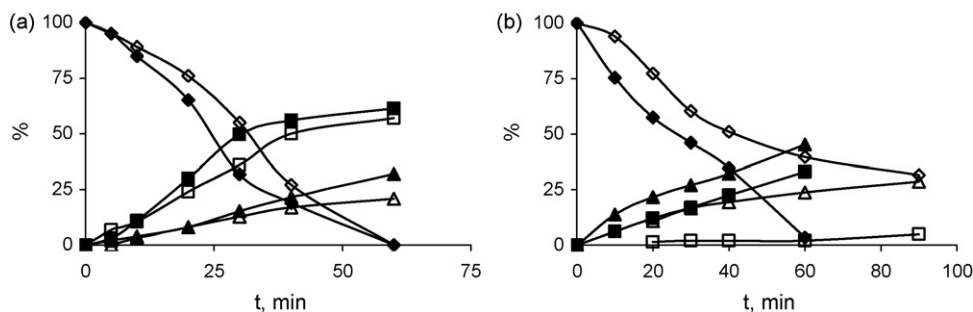
Fig. 5. (a) Photosensitized oxidation in acetonitrile of thioanisole (1c, diamonds) and formation of the corresponding sulfoxide (**2b**, triangles) and of diphenyl disulfide (**3c**, squares). Filled symbols, sensitizer TPT; empty symbols, TPT–HY. (b) The same oxidation in DCE. Filled symbols, sensitizer TPT–HY; empty symbols, TTPT–HY.

the appropriate geometry with the sulfur atom directed towards the inner part of the pore, must be progressively slowed along the series of the three aromatic sulfides considered, **1c–e**, particularly with the last two.

This is indeed observed. As an example, the ratio of the oxidation rate between TPT–HY and TPT is 0.64, 0.18 and 0.113 in DCE and 0.5, 0.06 and 0.2 in methanol for **1c–e**. About the same holds for TTPT–HY in comparison to TTPT, although with this sensitizer the values with **1d** and **1e** were at any rate lower than with the oxa analogue sensitizer. Since the oxidizing ability of the two sensitizers is similar [52] this suggests that the excited thiapyrylium interacts with the sulfides at a different geometry than does pyrylium, at least with the aromatic sulfides. It may be that with such derivatives TTPT interacts more with the ring than with the sulfur atom, resulting in a less effective sulfoxidation.

As for the solvent, there was a trend for a somewhat more effective oxidation in a polar/protic solvent such as methanol, but the effect was generally limited to 20–30%, except for the case of aliphatic **1a**, where it may arrive at a factor of 3 (see above). At any rate the solvent effect was virtually identical with soluble and immobilized sensitizers, confirming that the mechanism does not change with the immobilized sensitizers and that the characteristic limited dependence on experimental parameters of ET sensitized sulfide oxidation was maintained.

While the overall efficiency underwent a limited variation, the product distribution was more affected by the choice of the sensitizer, TP or TTP, its physical form and the solvent, in particular with aromatic sulfides. In the case of thioanisole (**1c**) as an example, the main product in acetonitrile with TPT was the sulfoxide. Photosensitization with TPT–HY was somewhat less efficient, but the course of the reaction and the product distribution remained the same (see Fig. 5). The reaction occurred at a comparable rate in DCE, with the disulfide as the main product, but with TTPT–HY the oxidation proceeded more slowly, tended to stop before complete oxidation of the sulfide and the amount of diphenyl disulfide was much lower than in MeCN (Fig. 5). This indicates that the matrix used for encapsulating the sensitizer has an influence not only on the first photochemical step (see Fig. 2) but also on the following course of the reaction. It is possible that polar/protic solvents wash away more easily the products formed from the zeolite, while with apolar solvent exchange of the substrates between

solution and adsorption in the cavities of the material is less efficient. The advantage remains, however, that the heterogeneous sensitizer is much more robust.

As one may have expected, the use of a sensitizer operating in the large cavities (3.4 nm) of mesoporous silica has no such dramatic effect. However, also in this case the oxidation of bulky sulfides is somewhat diminished, probably because the correct geometric approach between the sulfide and the sensitizer is somewhat hindered.

It may be also noticed that the photooxidation also takes place using a silica-adsorbed sensitizer, where however, the sensitizer itself and the sulfide rapidly equilibrate with the solution. The product distribution changes in some cases, though, reasonably due to the different adsorption of the primary photoproducts.

To conclude, we reported the use of zeolite immobilized pyrylium and thiapyryrylium sensitizers as convenient materials for the photosensitized oxidation of sulfides up to concentrations 0.05 M. Although the efficiency of the process does change depending on the nature of sulfide, sensitizer, solid host and solvent, the range of variations is much more restricted than with singlet oxygen and the immobilized sensitizers maintain the efficiency of the soluble counterpart, while being much more robust. The process has been carried out by using blue light as a model for solar light and largely prevents the sensitizer decomposition occurring with the same sensitizers in solution, and further takes advantage of the positive characteristics of heterogeneous catalysis, such as easy separation (and reuse) of the sensitizer, and minimizes contamination. The method therefore largely satisfies the requirements of generality and mildness and is suitable for decontamination purposes in the various applications reviewed in the introduction, although the occurrence of several competing processes makes synthetic application less easy, except for **1e** and presumably with all diaryl sulfides where the sulfoxide account for 80–90% of the products.

Simple geometric considerations explain the efficiency of immobilized sensitizers according to the ability of the sulfides of penetrating into the pores of the matrix. A particular case is the sensitized oxidation of aromatic sulfides by TTPT–HY that for not fully understood reasons is less efficient (a fact that may be exploited, if desidered, for the selective oxidation of aliphatic sulfides). In general, however, the simple comparison

of the geometry of substrates and pores is expected to apply to other substrates and be useful for planning the application of these materials to further photosensitized processes as well as for planning new heterogeneous materials.

Acknowledgements

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